

MECHANISM OF POLYMERIZATION OF METHYL METHACRYLATE USING CYCLOMETALATE COMPLEXES *cis*-[Ru(o-C₆H₄-2-(4-CH₃)py)(phen)(MeCN)₂]PF₆ AND *cis*-[Ru(o-C₆H₄-2-py)(phen)(MeCN)₂]PF₆

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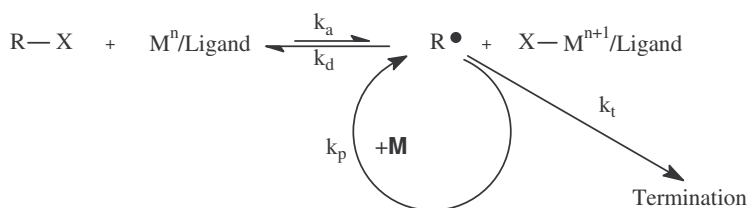
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Abstract- Atom transfer radical polymerization (ATRP) permits to obtain polymers and copolymers of low polydispersities and well-defined structures for a wide range of vinyl monomers [1-3]. Polymerization of MMA was promoted by the Ru (II) cyclometalated complexes with labile MeCN ligand in the presence and absence of Al(OiPr)₃. The polymerizations proceed via radical mechanism and requires the loss of MeCN ligand. The control of polymerizations can be explained in terms of the traditional ATRP scheme.

Introduction.

Since the pioneering works of M. Sawamoto and K. Matyjaszewski in 1995 [1,2] metal-catalyzed living radical polymerization (ATRP) has become one of the most intensively developed fields of polymer chemistry. The enormous progress made in the field is very impressive: polymer systems of controlled architecture and molecular weights have been synthesized with polydispersities of close to or even less than 1.1 [4,5]. The method is versatile and permits the use of all the advantages of conventional radical polymerization, such as mild reaction conditions, and a wide range of monomers and polymerizations may be conducted in bulk, solution or emulsion [4,]. The key reaction here is a reversible one-electron redox homolytic halogen abstraction by a transition metal catalyst from a halogen containing initiation, typically an alkyl halide, as is shown in scheme 1.



Scheme 1. ATRP reactions.

In order to suppress the termination and also to give an equal opportunity of propagation of all polymer chains, the reversibility should be very fast and the equilibrium should be significantly shifted to the right ($k_d \gg k_a$) allowing the dormant species to dominate in the system. Thus, the transitional metal complexes used for this purpose should be able to easily perform halogen abstraction and thus to be oxidized and then, rapidly return, at least in comparison with the propagation, to the original oxidation state. Therefore, it is preferable that the reduced or original state of the metal complexes should be more stable than its higher oxidation state. If the latter is not true and the metal prefers to stay in the higher oxidation state, the catalysts may be very active but control of the polymerization is poor and the process proceeds rather as an ordinary free radical polymerization. Different metals have been successfully used as

catalysts for ATRP, including Cu, Ru, Fe, Ni, Co, Pd with a variety of ligands [4]. The Cu complexes remain the most popular because of the low price of Cu, the relatively simple and the high activity and good controllability of the polymerizations of various vinyl monomers. In the proposed mechanism the catalyst activity is strongly correlated not only with the redox potential, but also with the halogenophilicity of the metal center. Ru (II) compounds for ATRP were first introduced by M. Sawamoto [1] and they are probably the second most frequently used catalysts. Recently, new cyclometalated Ru (II) compounds whose synthetic route is relatively simple and highly effective, have been reported [6]. Introduction of the metal-carbon σ -bond makes the complexes more robust and at the same time allows reducing their redox potential. Additionally some of the complexes demonstrate highly lability of acetonitrile ligands under certain conditions and thus species with much lower redox potentials have been generated. Thus it is interesting to examine these ruthenacycles with labile ligands as catalyst for ATRP. Here we report the application of two complexes, cycloruthenated compounds of 2-(p-tolyl) pyridine and 2-phenylpyridine, namely $\text{cis-}[\text{Ru}(\text{o-C}_6\text{H}_4\text{-2-(4-CH}_3\text{)py})(\text{phen})(\text{MeCN})_2]\text{PF}_6$ and $\text{cis-}[\text{Ru}(\text{o-C}_6\text{H}_4\text{-2-py})(\text{phen})(\text{MeCN})_2]\text{PF}_6$, further referred as $[\text{Ru}(\text{tolpy})(\text{phen})(\text{MeCN})_2]\text{PF}_6$ and $[\text{Ru}(\text{phpy})(\text{phen})(\text{MeCN})_2]\text{PF}_6$ (for their structures see figure 1), as catalysts for ATRP of methyl methacrylate (MMA). Other Ru complexes of the series are under investigation and the results will be reported soon.

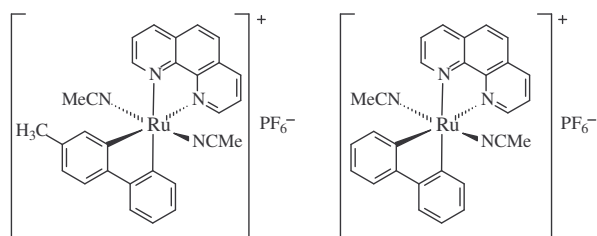


Figure 1. Catalysts for ATRP of MMA.

Experimental Section.

Materials. The monomer MMA was distilled under reduced pressure and kept under nitrogen, the others reagents and solvents were used as received from Aldrich Chem. Co. The synthesis and characterization of catalysts were detailed in the reference [11].

Polymerization Procedures. The polymerizations reactions were conducted in solution using $\text{Al}(\text{OiPr})_3$ and without it, using the Schlenk technique at 80°C . The Ru (II) complexes and the $\text{Al}(\text{OiPr})_3$ were degassed under vacuum and purged with nitrogen. Then the monomer was added via a syringe and the mixture was stirred 10-15 min until a homogeneous solution. Finally the initiator was added to the mixture. After this the Schlenk tube was submerged in an oil bath previously heated to 80°C . The samples were removed from the tube at certain time intervals using degassed syringes. After the polymerization reaction was stopped when the reaction mixture became viscous. The characterization of the samples was for GPC, these samples for GPC measurements were purified, first these were dissolved in ethyl acetate, the solution was passed through Florisil 60-100 mesh column and concentrated by rotary evaporation.

Results and Discussion.

The results obtained after of the experimental work are showed in the next tables:

Table 1.- Results of the reactions made with the catalyst [Ru(tolpy)(phen)(MeCN)₂]₂PF₆ using several initiators.

Reaction	Solvent	Initiator	Molar proportions M : C : I : A	Conv. (%)	Mn-t	Mn	D
1	Toluene	EBI	200: 1 : 1 : 0	43	9 000	21 149	1.28
2	Toluene	EBI	200: 1 : 1 : 4	78	16 000	27 970	1.63
3	Acetonitrile	EBI	200: 1 : 1 : 0	4	1 072	2 595	1.74
4	Acetonitrile	EBI	200: 1 : 1 : 4	9	1 904	4 338	2.16
5	Toluene	CCl ₄	200: 1 : 1 : 0	4	870	13 013	1.84
6	Toluene	CCl ₄	200: 1 : 1 : 4	37	7 000	7 094	2.45
7	Acetonitrile	CCl ₄	200: 1 : 1 : 0	4	1000	-----	-----
8	Acetonitrile	CCl ₄	200: 1 : 1 : 4	5	6 300	27 259	2.10
9	Toluene	BEB	200: 1 : 1 : 0	47	9 560	16 200	1.41
10	Toluene	BEB	200: 1 : 1 : 4	13	2 700	11 537	2.33
11	Acetonitrile	BEB	200: 1 : 1 : 0	4	1 000	-----	-----
12	Acetonitrile	BEB	200: 1 : 1 : 4	7	1 650	3 000	1.82

Table 2.- Results of the reactions made with the catalyst [Ru(phpy)(phen)(MeCN)₂]₂PF₆ using several initiators.

Reaction	Solvent	Initiator	Molar proportions M : C : I : A	Conv. (%)	Mn-t	Mn	D
1	Toluene	EBI	200: 1 : 1 : 0	58	11 850	26 211	1.28
2	Toluene	EBI	200: 1 : 1 : 4	71	27 840	31 602	1.80
3	Acetonitrile	EBI	200: 1 : 1 : 0	4	925	17 012	1.78
4	Acetonitrile	EBI	200: 1 : 1 : 4	8	1 795	14 477	1.83
5	Toluene	CCl ₄	200: 1 : 1 : 0	12	2 500	5 177	1.37
6	Toluene	CCl ₄	200: 1 : 1 : 4	22	4 500	9 027	1.21
7	Acetonitrile	CCl ₄	200: 1 : 1 : 0	4	918	-----	-----
8	Acetonitrile	CCl ₄	200: 1 : 1 : 4	2	4 190	6 000	2.01
9	Toluene	BEB	200: 1 : 1 : 0	55	11 160	21 795	1.37
10	Toluene	BEB	200: 1 : 1 : 4	73	14 730	30 832	1.46
11	Acetonitrile	BEB	200: 1 : 1 : 0	3	850	-----	-----
12	Acetonitrile	BEB	200: 1 : 1 : 4	5	1 220	2 295	1.06

After the reactions before, we decided to realize kinetics of the best system, there are two systems with good results using EBI and BEB as initiators in absence of aluminum isopropoxide and we decided study the system with BEB, toluene and without aluminum, varying the proportions of the initiator and the catalyst to observe the dependence or independence of the conversion and the molecular weight respect it. Only we made to [Ru(phpy)(phen)(MeCN)₂]₂PF₆ catalyst because of the results with the other are similar. The results obtained are show in the next table.

Table 3.- Results of the kinetics made with the catalyst [Ru(phpy)(phen)(MeCN)₂]₂PF₆ using BEB as initiator.

Reaction	M : C : I : A							
1	200 : 1 : 0.5 : 0	t(h)	1	2	3	4	5	6
		C(%)	14	26	27	28	29	30
		Mn-t	5 745	10 750	10 998	11 398	11 799	12 380
		Mn	10 447	12 708	16 112	13 332	11 836	12 928
		D	1.58	1.68	1.40	1.62	1.71	1.66
2	200 : 1 : 1 : 0	t(h)	1	2	3	4	5	6
		C(%)	26	45	56	63	65	----
		Mn-t	5 442	9 166	11 471	12 846	13 161	----
		Mn	7 692	9 978	10 888	11 354	10 227	----
		D	1.65	1.66	1.71	1.72	1.89	----
3	200 : 1 : 2 : 0	t(h)	1	2	3	4	5	6
		C(%)	49	57	61	69	73	82
		Mn-t	5 123	5 887	6 338	7 094	7 474	8 373
		Mn	3 914	4 443	4 425	4 450	45 54	5 028
		D	1.47	1.42	1.45	1.45	1.45	1.46
4	200 : 0.1 : 1 : 0	t(h)	3	6	9	12	27	30
		C(%)	15	16	17	18	19	20
		Mn-t	3 189	3 389	3 589	3 789	3 990	4 190
		Mn	6 575	6 714	6 775	6 764	6 748	6 815
		D	1.55	1.54	1.54	1.54	1.54	1.53
5	200 : 0.5 : 1 : 0	t(h)	1	2	3	4	5	6
		C(%)	13	30	39	44	49	51
		Mn-t	2 719	6 288	8 009	9 048	9 942	10 443
		Mn	5 367	8 153	9 057	9 524	9 695	9 301
		D	1.61	1.56	1.55	1.55	1.56	1.55
6	200 : 1 : 1 : 0	t(h)	1	2	3	4	5	6
		C(%)	26	45	56	63	65	----
		Mn-t	5 442	9 166	11 471	12 846	13 161	----
		Mn	7 692	9 978	10 888	11 354	10 227	----
		D	1.65	1.66	1.71	1.72	1.89	----

Where: M: Monomer, C: Catalyst, I: Initiator, A: Aluminum isopropoxide, Mn-t: *Theoretical* number average degree of polymerization, Mn: *Experimental* number average degree of polymerization, D: Polydispersity, EBI: Ethyl 2-Bromoisobutirato, CCl₄: Carbon tetrachloride, BEB: 1-Bromo ethyl benzene.

Like we can observe in the table 1 and in the table 2, all the reactions whose using aluminum isopropoxide as activator agent, the conversion is more high than the others this result is expected because of the activity of this Lewis acid whose function is activate the initiation of the polymerization an increase its rate, but all the others where we don't use aluminum isopropoxide we obtained enough conversions so it's an important result because the absence of aluminum isopropoxide into the mixture diminishes the difficult to understand the mechanism of initiation except when we use acetonitrile as solvent or CCl₄ as initiator. First when we use acetonitrile as solvent

practically there isn't reaction it's an evidence that in the mechanism of initiation is involved the acetonitrile as ligand labile or interchangeable with the halogen from the initiator via oxidative addition. In another hand when we use carbon tetrachloride as initiator the situation is more complex because it compound can give one or two radicals from one molecule of carbon tetrachloride and it makes more difficult to understand the mechanism of initiation. Now analyzing the results of the kinetics reactions shown in the table 3 made using BEB as initiator varying the molar proportions of the initiator and catalyst, we can observe that in all reactions the tendency is like controlled radical polymerization except in the reaction 1 with 0.5 of initiator the best are with 200 /1/1 proportions (reactions 2 and 6) and with 200/1/0.5 proportions (reaction 5) the possible mechanism is show in the conclusions.

Conclusions.

We realized studies of the polymerization with aluminum isopropoxide and without it using cyclometalate compounds of ruthenium (II) and is possible realize the polymerization of methyl methacrylate in absence of the aluminum isopropoxide and with aluminum isopropoxide $\text{Al}(\text{OiPr})_3$, and the possible mechanism of the reaction is via oxidative addition of the halogen from the initiator toward metal center substituting one acetonitrile ligand.

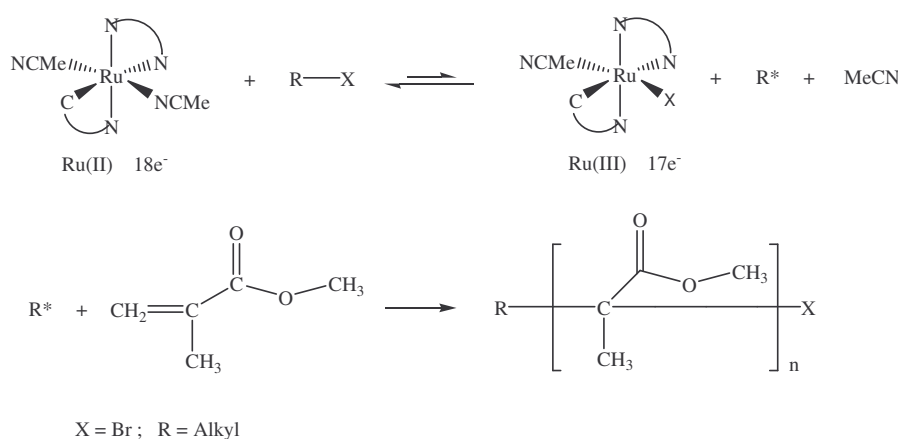


Figure 2. Mechanism of initiation of the polymerization of MMA.

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